

INTEGRATED EXPERIMENTS TO DEMONSTRATE INNOVATIVE REPROCESSING OF METAL AND OXIDE FUEL BY MEANS OF ELECTROMETALLURGICAL TECHNOLOGY

T. KOYAMA^a, T. HIJIKATA^a, T. INOUE^a,
M. MYOCHIN^b, S. KITAWAKI^b, T. SHINOZAKI^b

^aPyro-process fuel cycle project
Central Research Institute of Electric Power Industry (CRIEPI)
Tokyo, Japan

^bAdvanced fuel recycle technology division
Japan Nuclear Cycle Development Institute (JNC)
Ibaraki, Japan

Abstract. Electrometallurgical pyro-processing is a key innovative technology to realize closed actinides cycle with keeping high proliferation-resistance and economy. The current status and the strategy of development of the electrometallurgical pyro-processing technology are summarized, and the necessity to demonstrate whole process in one continuous operation is stressed. The test titled “integrated experiments of electrometallurgical reprocessing of metal and oxide Pu-containing fuel” has been jointly started by CRIEPI and JNC. The new glove box system equipped with pyro-process apparatuses such as electrorefiner was developed and installed in CPF of JNC-Tokai Works. The test will enable us to evaluate the technical feasibility of this process to apply closing actinides cycle.

1. INTRODUCTION

Dry (i.e., non-aqueous) processing technologies are currently being focused in many countries for closing actinide fuel cycle because of their favorable economic potential [1] and an intrinsic proliferation-resistant features due to inherent difficulty of extracting weapons-usable plutonium [2]. Electrometallurgical technology (pyro-process) originally developed for metal fuel by Argonne National Laboratory (ANL) [3] is one of the most attractive dry processing technologies, because it has an inseparability properties of Pu from other actinides in any step of the process [4]. This property enables us to enhance intrinsic proliferation resistance in addition to recovery of long-lived transuranium elements for transmutation in the reactor without addition of further treatment. Intensive fundamental studies in many organizations such as CRIEPI[5], ITU[6], BNFL&CEA[7], etc. as well as the development to engineering scale in ANL such as the test to treat spent EBR-II fuel[8] have demonstrated high potentiality to industrialize.

Inseparability of plutonium from other actinides in the refining step of pyro-process is theoretically guaranteed by the thermodynamic properties such as the distribution of actinides in the molten salt and liquid cadmium system expressed as follows,

$$SF_M(\text{Pu}) = \frac{[X_M]_{\text{salt}}}{[X_M]_{\text{cd}}} \cdot \frac{[X_{\text{Pu}}]_{\text{salt}}}{[X_{\text{Pu}}]_{\text{cd}}} = \frac{[\gamma_{\text{Pu}}]_{\text{salt}}}{[\gamma_{\text{Pu}}]_{\text{cd}}} \cdot \frac{[\gamma_M]_{\text{cd}}}{[\gamma_M]_{\text{salt}}} \cdot \exp\left[-\frac{\Delta G_f^\circ \text{MCl}_3 - \Delta G_f^\circ \text{PuCl}_3}{RT}\right], \quad (1)$$

where $[X_i]_j$ denotes the concentration of i in phase j . Notation of this equation follows the ordinal expression of thermodynamics. The distribution data set of the actinides, U, Np, Pu, Am, and Cm, was first reported by one of the authors in 1992 [9] as Table I. It shows clearly the recovery of plutonium shall take place simultaneously with the recovery of other actinides with keeping the separation of fission products such as lanthanides.

Applicability of the electrometallurgical technology to treat other fuel types such as oxide fuel, nitride fuel, MOX fuel, etc. is another attractive feature. Conversion technology such as Li reduction [10] enables to feed oxide fuel into electrometallurgical pyro-process. Figure 1 shows the example of reduced metal from simulated spent MOX fuel with Li reductant carried out by one of the authors [11]. Nitride fuels are found to be processed in the electrometallurgical technology without major reformation of the process [12].

The molten salt media also gives two important advantageous properties as a solvent material in nuclear processing. The radiation stability of molten salt allows the processing of spent fuels of high radioactivity (e.g. spent fuel with short cooling time) without any increase of the solvent waste. Since molten salt is not a neutron moderator such as water is, comparatively large amount of fissile material can be handled in the process equipment, i.e. experimental facilities are compact and economical.

The major wastes specific to pyro-process are the salt waste and the metal waste. The salt waste must be immobilized into water-insoluble form. Several immobilization methods have been proposed[13,14], and immobilization in the glass bonded sodalite form was demonstrated with irradiated fuel treatment[15]. Consistency of the metal waste form has also been studied with simulated waste[16].

Table I. Measured separation factors (SF) of actinides from Pu in LiCl-KCl/Cd system [9]

Element	Separation Factor
U	0.532
Np	1.13
Pu	1.00 (basis)
Am	1.64
Cm	1.87
Ce	24
Nd	21

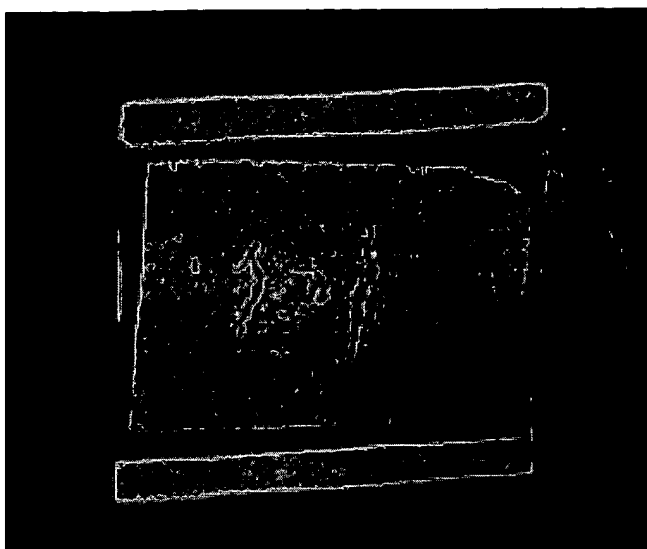


FIG. 1. Reduced metal from MOX [11].

2. CLOSING ACTINIDES CYCLE WITH PYRO-PROCESSING TECHNOLOGY

Central Research Institute of Electric Power Industry (CRIEPI) has been proposing the “actinide recycling by pyro-process with fast breeder reactor” [5], where metal fueled FBR is combined with pyrometallurgical reprocessing, pyrochemical reduction of oxide fuel into metal form, and pyro-partitioning of TRUs from HLW of PUREX reprocessing of LWR fuel. The concept is schematically described in Fig. 2, where the processes with pyro-processing technology are noted with red letters. As seen in this figure, pyro-processing technology can be applied to fill up the gap between two cycles as well as to close FBR fuel cycle itself. The detail of each application is summarized in this section with the technical basis developed by CRIEPI

CRIEPI started the study on actinide recycling technology on 1985 including the joining in IFR Project of US-DOE from 1989 to 1995. Pyro-partitioning of TRU and transmutation [17] was nominated to the OMEGA project (long-term research/development program for the long-lived nuclides partitioning and transmutation) of Japan. The project shared by Japan Atomic Energy Research Institute(JAERI), Japan Nuclear Cycle Development Institute(JNC) and CRIEPI was checked and reviewed on 1999 by Japanese Atomic Energy Commission. On 1998, CRIEPI and JRC-ITU started joint study to demonstrate the feasibility of each actinide recycling process with using real spent fuel and real HLW [18].

In the *FBR fuel cycle* of Figure 2, metal fuel consists of U-Pu-Zr and U-Zr alloys are fabricated by the injection casting process that allows remote handling and high MA content. Technical feasibility of 20 kg U-10Zr batch fuel casting[19] and the allowable amount of MA in U-Pu-MA-RE-Zr[20] have been confirmed experimentally by CRIEPI. The irradiated metal fuel is reprocessed by pyro-reprocessing. The chopped spent fuel is anodically dissolved in LiCl-KCl molten salt *electrorefining process* (Fig. 3), and U-Pu and U are recovered to the liquid Cd cathode and the solid iron cathode, respectively. The U-Pu products of the process contain MAs and rare earth fission products according to the electropotentials shown in Fig. 4[21]. The recovery of U, Pu and Am from U-Pu(Am)-Zr fuel[22] as well as the basics of molten salt electrorefining[23,24] has been studied. The accompanied media, salt and Cd, are

to be removed from U-Pu-MA or U products by distillation at the *cathode process* (Fig. 5). The obtained U-Pu-MA or U ingot is casted into quartz mold to make metal slugs at injection casting fuel fabrication. On the other hand, the fission products remained in the salt or metal phase are recovered and converted into the ceramic waste [14] or metal waste.

The oxide fuels such as UO_2 and MOX can be treated in the above mentioned FBR cycle after reduction to metal form as Figure 2. The *Li reduction process* using Li metal reductant has been intensively studied by CRIEPI[11,25,26]. As shown in Fig. 6, dissolved Li react with oxide to form Li_2O in the LiCl molten salt at 650°C . The feasibility of this process has already been demonstrated with UO_2 [25], MOX [11] and single MA oxide like AmO_2 [26].

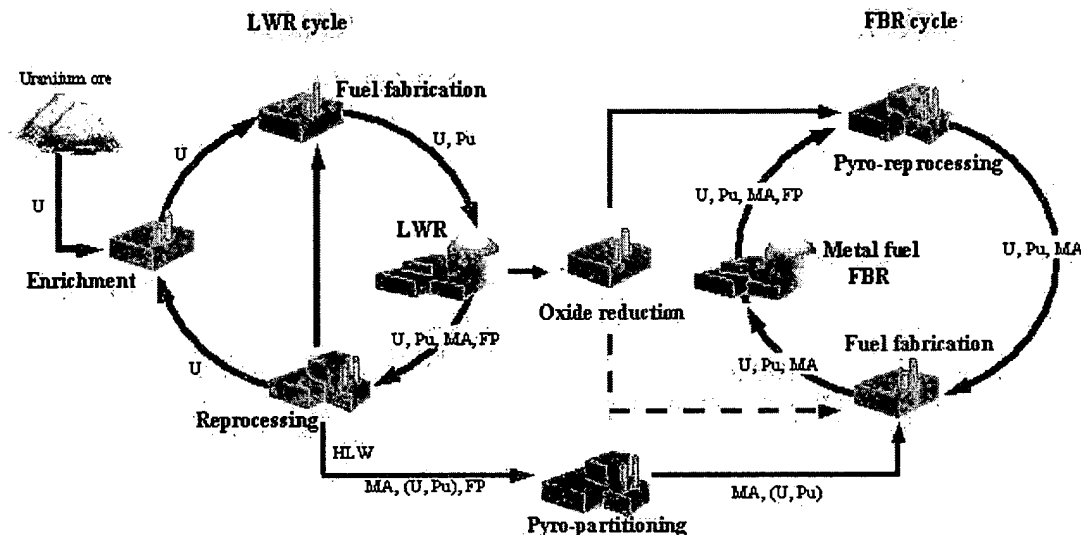


FIG. 2. CRIEPI's concept to close the actinides cycle by applying pyro-technology.

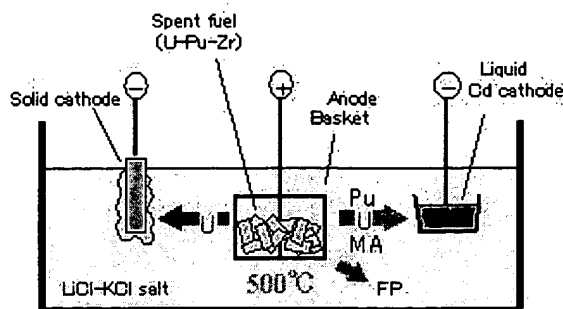


FIG. 3. Electrefining process.

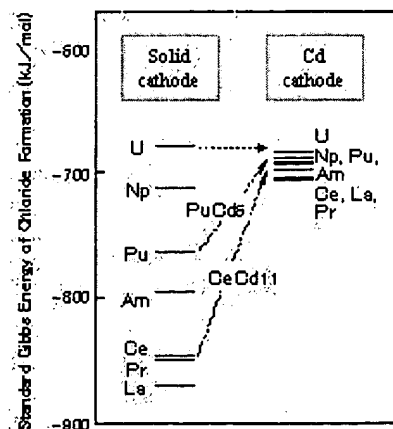


FIG. 4. Reduction potentials in LiCl-KCl .

BEST AVAILABLE COPY

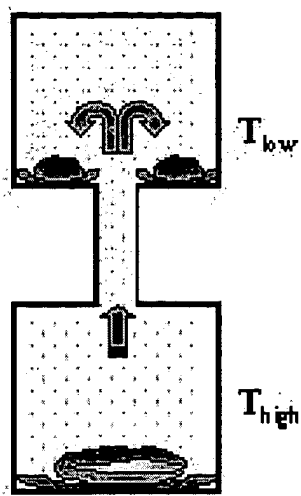


FIG. 5. Cathode processing.

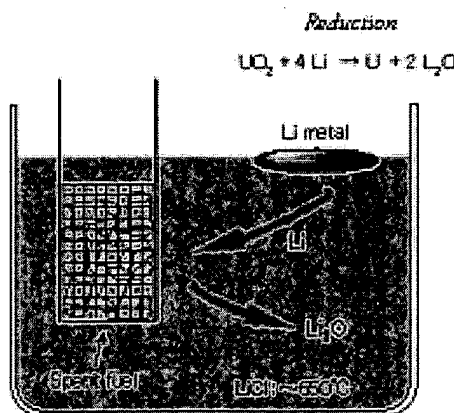


FIG. 6. Li reduction of oxide fuel.

The *pyro-partitioning* of TRUs from HLW of PUREX reprocessing of LWR fuel is also adopted as shown in Fig. 2. The HLW is converted into chloride through chlorination, and TRUs are extracted by molten salt extraction process followed by eletro-recovery. The feasibility of the pyro-partitioning has already been demonstrated with unirradiated TRUs [27, 28]. The test with real HLW is now under study [18].

3. FEASIBILITY STUDY OF FAST REACTOR CYCLE SYSTEM

At 1998, JNC and utilities agreed to start studying jointly to establish a commercialization concept which maximizes economic competitiveness while ensuring the highest levels of safety[29]. The study was named as “Feasibility study of commercialized fast reactor systems“, and consists of 3 phases listed below.

- **Phase 1 (1999-2000)** Evaluate a wide variety of technical options introducing innovative technologies and select several useful concepts and prepare necessary R&D schedule.
- **Phase 2 (2001-2005)** A well-balanced consistency between FR system and its fuel cycle is pursued for FR cycle candidate concepts screened in Phase 1. Promising commercialized FR cycle candidates (2 or 3) are determined through design studies and engineering tests.
- **Phase 3+(2006-2015)** Conduct the study with Check & Review every 5 years and present FR cycle technology with the technical data in around 2015

In order to achieve the objective of each phase, this study is being carried out with the participation of all parties concerned in Japan, i.e., the electric utilities, CRIEPI, and JAERI.

Key technologies for advanced fuel cycle system have been proposed and reviewed. As the end of phase-1, several candidate technologies were screened and selected by preliminary assessment. As the advanced reprocessing candidates, dry processing such as the electrometallurgical process and the oxide electrowinning process have been selected in addition to the aqueous processes.

In the study of advanced fuel cycle technology, R&D of the electrometallurgical technology has been designated to CRIEPI. The technical achievement of CRIEPI are reviewed in the feasibility study. In the course of this study, the importance to carry out the electrometallurgical processing test with using plutonium was recognized. Because the recovery of transuranics has been examined only for each step [18] or U based fuels [8, 30], it is necessary to test whole process in one continuous operation with using Pu-containing fuel. Hence, CRIEPI and JNC have agreed to start new joint study to implement the integrated experiments of electrometallurgical reprocessing of metal and oxide Pu-containing fuel at *chemical processing facility* (CPF) of JNC-Tokai Works [31].

4. INTEGRATED EXPERIMENTS TO DEMONSTRATE REPROCESSING OF METAL AND OXIDE FUEL BY MEANS OF ELECTROMETALLURGICAL TECHNOLOGY

4.1. Test schedule and process to demonstrate

The electrometallurgical process selected for the integrated experiments is shown in Fig.7. It consist of (1) reduction of oxide fuel into metal form by means of Li reductant, (2) molten salt electrorefining to recover U and U-Pu, (3) cathode process to remove salt and Cd from actinides, (4) injection casting of actinide to form metal fuel, and (5) oxidation of actinide to form oxide fuel. As shown in the same figure, the experiments proceeds in the order of (2), (3), (4) for metal fuel reprocessing and (1), (2), (3), (5) for oxide fuel reprocessing, respectively.

The time schedule of this study is shown in Table II. In year 2002, the apparatus was finished installing, and the cold test with non-radioactive simulants started. The integrated test with uranium is planned on 2003, and followed by the test with plutonium. As shown in this figure, we are now in the phase of cold & uranium test. In the course of process experiments, development of auxiliary technology such as nuclear material management and waste management are carried out in order to evaluate the technology to realize electrometallurgical reprocessing.

4.2. Apparatus development

The new glove box system has been developed, and installed at CPF. It consists of one process glove box with an Ar purification unit and two air glove boxes(see Fig.8). The atmosphere of Ar glove box is kept in less than 10ppm of O₂ and H₂O impurities for avoiding the deterioration of molten salt and recovered metals. The radiation-shielded heating wells are placed on the bottom of the box to install process equipments such as electrorefiner. Up to 220g of Pu(+U²³⁵) and 2.22*10⁸Bq of fission products can be handled in this box.

The process equipments are developed based on the study of CRIEPI (see chapter 2), and of JNC [32]. The installed Li reduction apparatus is shown in Fig. 9. Small tungsten crucible charged with oxide is immersed in the LiCl bath contained in the larger crucible. About 20 g of MOX will be reduced in this apparatus. The installed electrorefiner is shown in Fig. 10. It consists of a steel crucible of 120 mm diameter for salt electrolyte and three electrodes, an anode, a cathode and a reference electrode. Two different cathodes, a solid cathode and a liquid Cd cathode, are designed to use each other. The anode assembly is designed to charge the reduction crucible for anodic dissolution of the reduced oxide. The installed cathode processor is shown in Fig. 11. The deposit from the electrorefiner is charged in a graphite crucible to be induction heated, and the vaporized salt and Cd is recovered at the condenser-collector located above the graphite crucible. The recovered U-Pu or U from cathode

processor is charged into another graphite crucible for same induction heating, and the melt is injection casted into the quartz mold for obtaining slug samples. The oxidation of metal with Ar-O₂ gas is carried out in the apparatus shown in Fig. 12.

In year 2002, the installation of apparatus was completed, and the internal safety review to start active experiments with U and Pu is underway.

Table. II. Time schedule of the integrated experiments

4.2.1.1. JPN FY	2000	2001	2002	2003	2004	2005
Licensing, design & installation						
Process experiments			Cold & U test		Pu test	
Auxiliary technology development						

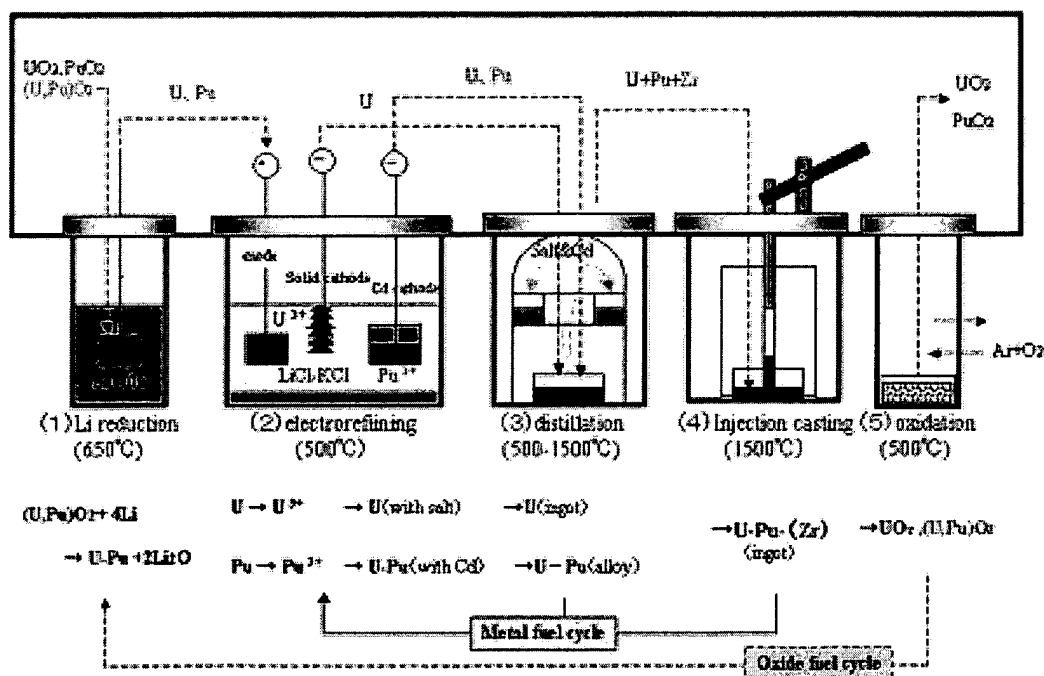


FIG. 7. Electrometallurgical process for the integrated experiments.

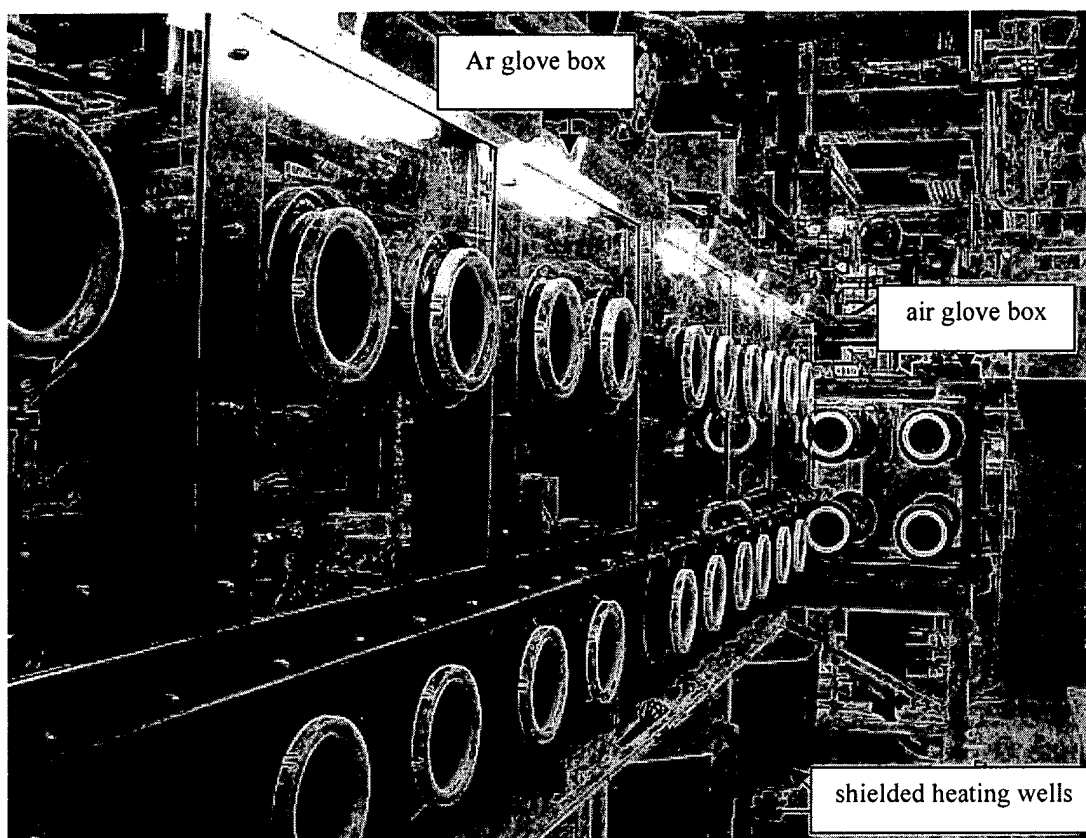


FIG. 8. New glove box system for integrated experiments with electrometallurgical technology.



FIG. 9. Li reduction apparatus.

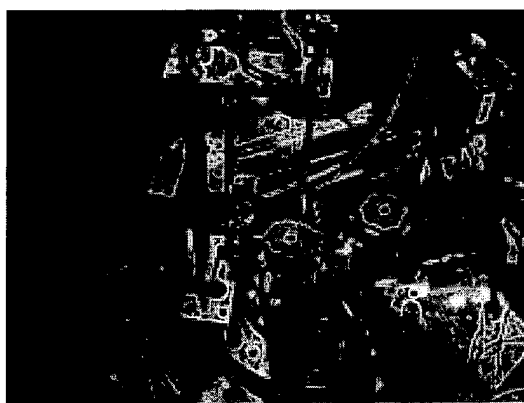


FIG. 10. Electrorefining apparatus.

BEST AVAILABLE COPY

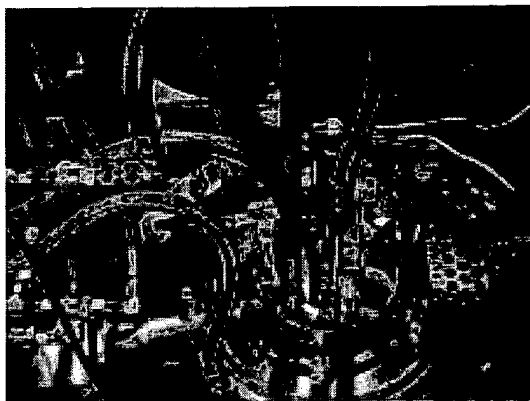


FIG. 11. Cathode processing apparatus.

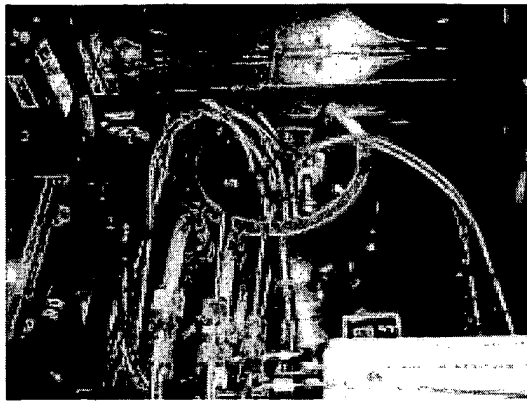


FIG. 12. Oxidation apparatus.

4.3. Integrated test with non-radioactive simulants

As the first step to implement the integrated experiments, non-radioactive materials that simulate actinide behavior in each step were selected. In the course of this experiments, the integrity of experimental procedure as well as the function of apparatus were confirmed as follows.

In the Li reduction process, TiO and Fe_3O_4 were selected for UO_2 simulants. Obtained reduction ratio of TiO in one experiment was about 85%, though Fe_3O_4 was reduced almost completely. The difficulty of reduction of TiO compared with Fe_3O_4 was as expected because of the difference of diffusion coefficient and thermodynamic stability. The complete reduction of actinide oxides is expected in the same experimental condition according to the study of CRIEPI [25,26].

In the electrorefining process, titanium and cerium was selected for U, Pu simulants. Metal cerium was charged into the anode basket, then electro-transported to either solid iron cathode or liquid Cd cathode. Fig. 13 shows the obtained deposit consists of metal cerium and entrained salt. The measured faradaic efficiencies are about 100 % at both electrodes. The reduced TiO obtained in the Li reduction experiment was then charged into the electrorefiner as an anode, and a metallic deposit was recovered at the solid iron cathode.

In cathode process, cerium deposit obtained in the electrorefining process was charged. The entrained salt was distilled off at around 1000°C with leaving cerium metal in the crucible. Distillation of salt-Cd mixture was also examined for simulating Cd cathode deposit. About 100% of salt and Cd were recovered in the condenser-collector as shown in Fig. 14.

In the oxidizing process, metal cerium was oxidized with Ar-O_2 gas at around 500°C . Complete oxidation was confirmed by weight increase and X-ray diffraction.

BEST AVAILABLE COPY

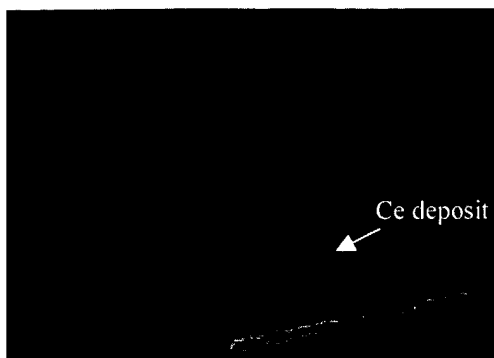


FIG. 13. Solid cathode deposit (Ce).

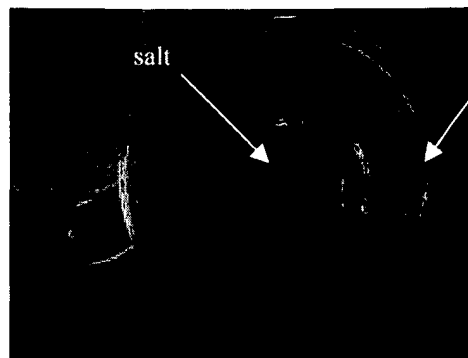


FIG. 14. Recovered salt and Cd by cathode process.

5. CONCLUSION

In order to demonstrate an innovative technology to close actinide cycle, called *electrometallurgical pyro-processing*, CRIEPI and JNC has started new joint study to implement an integrated experiments of electrometallurgical reprocessing of metal and oxide Pu-containing fuel. The new experimental apparatus dedicated for this experiment has been installed in CPF of JNC-Tokai Works. The apparatus is now under internal safety review to start active experiments with actinides such as U and Pu. Integrity of the experimental procedure as well as the function of apparatus was confirmed by the experiments carried out with non-radioactive simulants. After start operation with actinides, this test will enable us to evaluate the technical feasibility of this process to apply closing actinides cycle.

6. REFERENCES

- [1] TANAKA, HIROSHI et al., "Design study on advanced reprocessing systems for FR fuel cycle," GLOBAL2001, September 2001, Paris, 054(2001).
- [2] USDOE, TOPS task force of the Nuclear Energy Research Advisory Committee (NERAC), "Technological opportunities to increase the proliferation resistance of global civilian nuclear power systems", January 2001
- [3] CHANG, Yoon I., "The integral fast reactor", Nuclear Technology, 88, 129(1989).
- [4] GARCIA, H.E., et al., "Proliferation resistance of advanced sustainable nuclear fuel cycles", Proceedings of GLOBAL2001, September 2001, Paris, 299(2001).
- [5] INOUE, TADASHI, "Actinide recycling by pyro-process with metal fuel FBR for future nuclear fuel cycle system", Progress in Nuclear Energy, Vol.40, No.3-4, 547-554,2002
- [6] GLATZ, JEAN-PAUL, et al., "Advanced reprocessing research at ITU", Proceedings of GLOBAL2001, September 2001, Paris, 113(2001).
- [7] DONALDSON, N., et al., "Pyrochemistry- from flow sheet to industrial facility", ibid, 193(2001).
- [8] BENEDICT, ROBERT et al., "Progress in electrometallurgical treatment of spent nuclear fuel", J.Nuclear Science and Technology, Supplement 3 (Proceedings of Actinide2001), p749.
- [9] KOYAMA, TADAFUMI, JOHNSON, TERRY R., FISCHER, DON F., "Distribution of actinides between molten chloride salt / cadmium metal systems", J. Alloys and Compounds, 189, 37(1992).
- [10] BATTLES, JAMES E., et al., MISHRA, B. ed., "Actinide Processing: Methods and Materials", The Minerals, Metal & Materials Society, 135(1994).

- [11] USAMI, TSUYOSHI et al., "Behavior of actinide elements in the lithium reduction process (2) - Determination of the condition to reduce Am and Np, and evaluation of the reduction behavior of MOX pellet", CRIEPI Report(in Japanese), T00020, April 2001.
- [12] SHIRAI, O. et al., "Recovery of U by electrolysis in LiCl-KCl eutectic melts", *ibid*, p745, November 2002.
- [13] ACKERMAN, JOHN P., et al., "Treatment of wastes in the IFR fuel cycle", *Progress in Nuclear Energy*, 31, 141(1997).
- [14] KOYAMA, TADAFUMI, et al., "Waste form development for immobilization of radioactive halide salt generated from pyrometallurgical reprocessing", *Proceedings of GLOBAL'97*, Yokohama, October 1997.
- [15] SIMPSON, M.F., et al., "A description of the ceramic waste form production process from the demonstration phase of the electrometallurgical treatment of EBR-II spent fuel", *Nuclear Technology*, 134, 263(2001).
- [16] JOHNSON, S.G., et al., "Long-term immersion test results of the metallic waste form from the EMT process of EBR-II spent metallic fuel", *Proceedings of the fifth Topical Meeting on DOE Spent Nuclear Fuel and Fissile Materials Management*, Charleston, SC, September 17-20, 2002.
- [17] INOUE, TADASHI, et al., "Development of partitioning and transmutation technology for long-lived nuclides", *Nuclear Technology*, 69, 206(1991).
- [18] KOYAMA, TADAFUMI et al., "Demonstration of pyrometallurgical processing for metal fuel and HLW", *Proceedings of GLOBAL2001*, September 2001, Paris, 170(2001).
- [19] TOKIWAI, MORIYASU, et al., "Development of fabrication technology of metallic fuel by injection casting", *J.Nuclear Science and Technology*, Supplement 3 (*Proceedings of Actinide2001*), p910, November 2002
- [20] INOUE, Tadashi, et al., "Characterization of fuel alloys with minor actinides", *Trans. Am. Nucl. Soc.*, 64, 552(1991).
- [21] SAKAMURA, YOSHIHARU, et al., "Measurement of standard potentials of actinides (U,Mp,Pu,Am) in LiCl-KCl eutectic salt and separation of actinides from lanthanides by electrorefining", *J. Alloy. Comp.*, 271-273, 592(1998).
- [22] KOYAMA, TADAFUMI et al., "Study of molten salt electrorefining of U-Pu-Zr alloy fuel", *J.Nuclear Science and Technology*, Supplement 3 (*Proceedings of Actinide2001*), p765, November 2002.
- [23] KOYAMA, TADAFUMI et al., "An experimental study of molten salt electrorefining of uranium using solid iron cathode and liquid cadmium cathode for development of pyrometallurgical reprocessing", *J. Nucl. Sci. Technol.*, 34, 384(1997).
- [24] IIZUKA, MASATOSHI, et al., "Actinides recovery from molten salt/liquid metal system by electrochemical method", *J. Nuclear Materials*, V247, 183-190(1997).
- [25] USAMI, TSUYOSHI, et al., *J. Nucl. Mater.*, 300, 15(2002).
- [26] USAMI, TSUYOSHI, et al., submitted to *J. Nucl. Mater.*
- [27] KURATA, M., et al., "Conversion of high level waste to chloride for pyrometallurgical partitioning of minor actinides", *Proceedings of 7th Int. Conf. On Radioactive Waste Management and Environmental Remediation, ICEM'99*, Nagoya, 26-30 September, 1999.
- [28] KINOSHITA, KENSUKE, et al., "Separation of uranium and transuranic elements from rare earth elements by means of multistage extraction in LiCl-KCl/Bi system, *J. Nucl.Sci.Technol.*, 36, 189(1999).
- [29] NODA, HIROSHI, et al., "Feasibility study on commercialized FR cycle system in Japan -The results in the first phase and future plans of the study-", *Proceedings of GLOBAL2001*, September 2001, Paris, 052(2001).

- [30] TOKIWAI, MORIYASU et al., "Development of metallic uranium recovery technology from uranium oxide by Li reduction and electrorefining", *ibid*, p917.
- [31] NOMURA, SHIGEO, et al., "Development of challengeable reprocessing and fuel fabrication technologies for advanced fast reactor fuel cycle", *ibid*, 042(2001).
- [32] KITAWAKI, SHINICHI, et al., "Evaluation of pyrochemical reprocessing technologies for practical use", *Proc. Workshop on Pyrochemical Separation*, 14-16 March, 2000, Avignon, France, p87.